

Investigation of Alkali Salts with the STA 449 *F5 Jupiter*[®]

Dr. Alexander Schindler and Dr. Michael Schöneich



Introduction

While analytical techniques such as EDX or ICP-MS provide a detailed analysis of chemical elements, e.g., of those occurring in a salt sample [1], methods of thermal analysis can be used to also identify and characterize different chemical compounds present in such a sample. Simultaneous thermal analysis (STA), which refers to thermogravimetry (TGA) and differential scanning calorimetry (DSC) simultaneously performed in one experiment, was, for example, employed to investigate cement raw materials including the presence and impact of alkali metal salt impurities [2]. Another example is the melting process and the specific heat capacity of the phase change material (PCM) sodium nitrate, NaNO_3 , which was studied by means of DSC [3].

This work deals with STA measurements on NaCl, KCl, usual table salt and so-called Himalayan salt where the melting, partial evaporation and compositional analysis of the salts are the focus. Alkali salts like NaCl (halite) and KCl (sylvite) play an important role in our day-to-day life. While NaCl is the main component in table or cooking salt, KCl can, for example, be used as road salt in winter. Himalayan salt originating from Pakistan is a natural salt that contains – along with NaCl – various minerals and oxides like Fe_2O_3 [1], which is responsible for the slightly pink color (see photo above).

Experimental

Measurements were carried out using the STA 449 *F5 Jupiter*[®] (see figure 1). This instrument, which has an SiC



1 NETZSCH STA 449 *F5 Jupiter*[®] equipped with an optional automatic sample changer (ASC)

furnace allowing a maximum sample temperature of 1600°C, can optionally be equipped with the automatic sample changer (ASC) and coupling techniques for evolved gas analysis such as MS, FT-IR or GC-MS. The weighing range of the balance is as wide as 35 g with a balance resolution of 0.1 µg over the entire range. Another advantage of the STA 449 *F5 Jupiter*[®] is the TG-BeFlat[®] software functionality which automatically takes the buoyancy effect

into account so that baseline measurements are no longer necessary for standard tests.

The measurement conditions applied for this work are summarized in table 1.

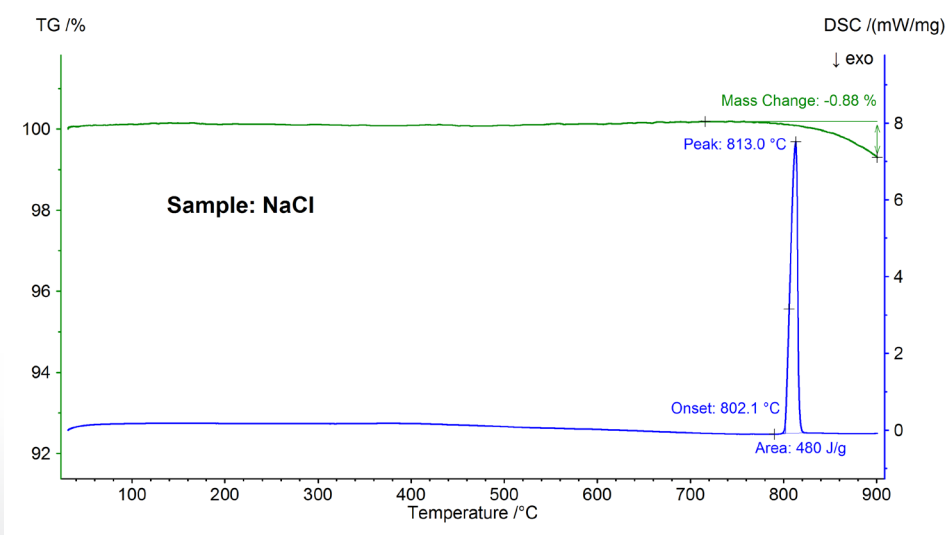
Samples NaCl [4] and KCl [5] both had nominal purities of 99.8% whereas no information regarding the purity was available for the table salt and the Himalayan salt. All samples were measured as a thin layer of grains just covering the bottom of the crucible; the sample material was neither ground nor compacted.

Results and Discussion

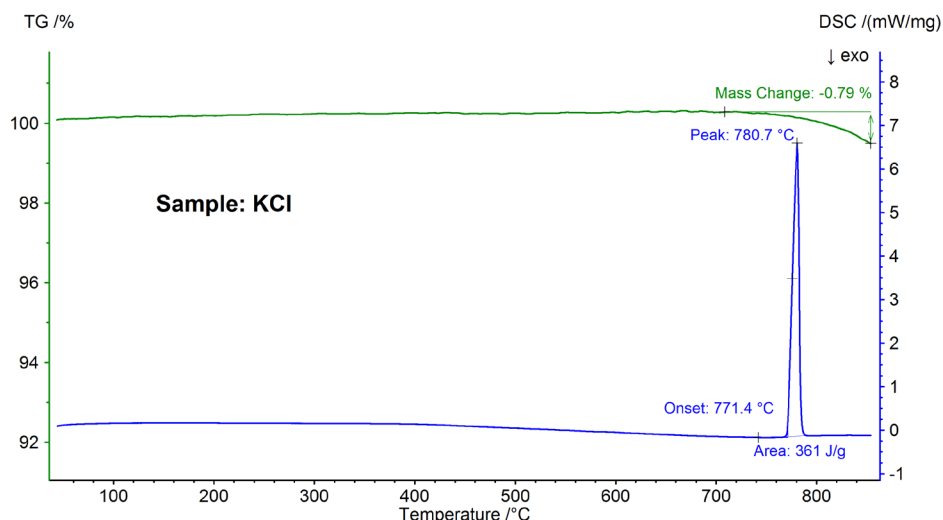
Depicted in figure 2 are the temperature-dependent mass change and heat flow rate of the NaCl sample. At an extrapolated onset temperature of 802.1°C, an endothermic effect with a peak temperature of 813°C and an enthalpy of 480 J/g was observed, which can be attributed to melting of the sample. The onset temperature, which reflects the melting point, matches well with the literature value of 801°C; the enthalpy of 480 J/g is also in good agreement with the heat of fusion value of 484 J/g found in literature [6]. Above about 800°C, a mass loss of 0.9% occurred, which is due to partial evaporation of the sample.

Tab. 1. Measurement conditions applied for this work

Measurement Conditions	
Instrument	STA 449 F5 Jupiter [®]
Sample carrier	TGA-DSC type S
Crucibles	PtRh (0.19 ml)
Heating rate	10 K/min
Sample masses	23 ± 1 mg
Atmosphere	N ₂
Purge gas flow rate	70 ml/min



2 Temperature-dependent mass change (TGA) and heat flow rate (DSC) of the NaCl sample

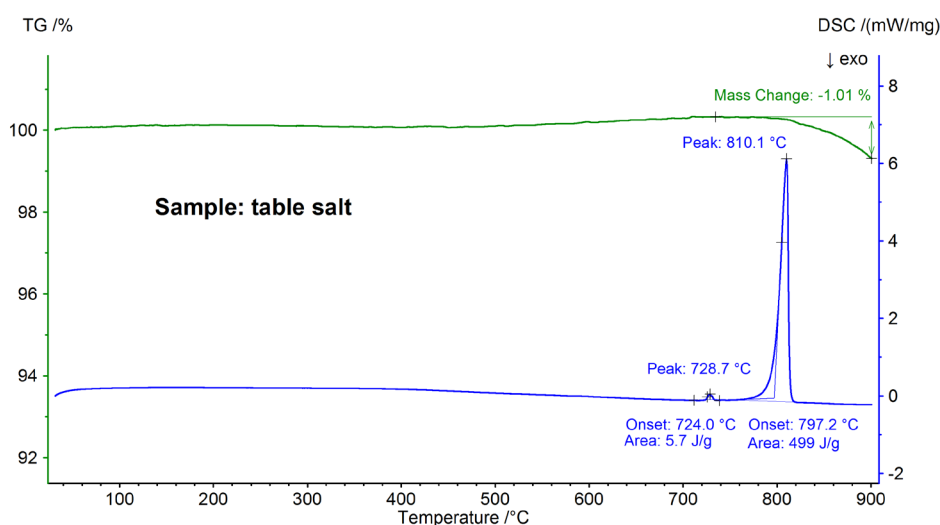


3 Temperature-dependent mass change (TGA) and heat flow rate (DSC) of the KCl sample

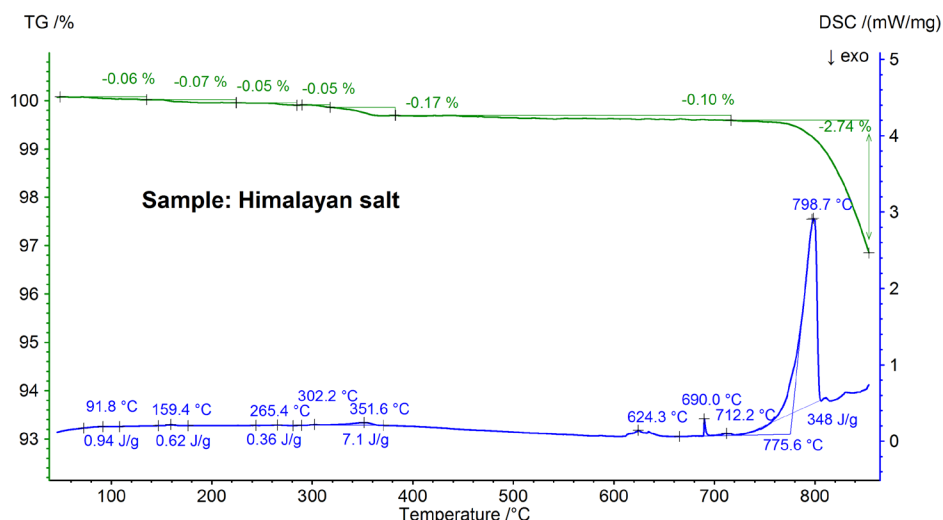
The STA results for the KCl sample are shown in figure 3. Again, melting and partial evaporation were observed; the melting point, detected at 771.4°C, is in good agreement with the literature value of 772°C and the enthalpy value of 361 J/g is again in accordance with the value of 351 J/g reported in the reference [6].

Displayed in figure 4 are the STA results obtained for the table salt sample, which clearly differ from the results obtained for the pure NaCl sample (compare figures 4 and 2): The onset of the main DSC peak is at 797.2°C and

thus significantly below the value of 802.1°C observed for pure NaCl; also, an additional endothermic effect was detected at an extrapolated onset temperature of 724°C. The enthalpy of the main melting effect of 499 J/g is in the same range as the value of 480 J/g observed for pure NaCl, whereas the enthalpy of the first effect is only 6 J/g. These results demonstrate that the table salt is – as expected – not pure NaCl; the DSC curve found for the table salt sample is typically observed for binary salt mixtures [7]. In this case, NaI-NaCl with a concentration of NaI in the lower percentage range is the most likely candidate [7].



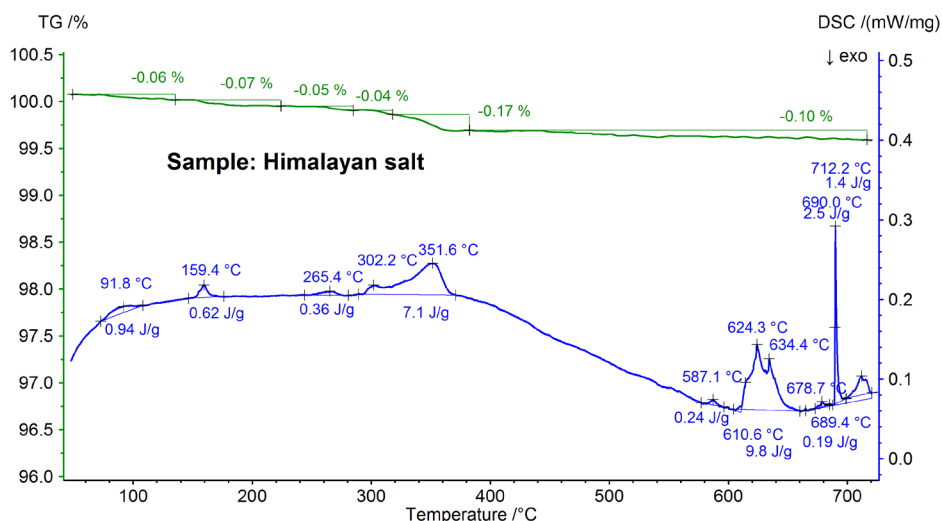
4 Temperature-dependent mass change (TGA) and heat flow rate (DSC) of the table salt sample



5a Temperature-dependent mass change (TGA) and heat flow rate (DSC) of the Himalayan salt sample

The STA results obtained for the Himalayan salt shown in figures 5a and 5b are even more complex than the results for the table salt. This can already be seen in the mass-loss steps of 0.06%, 0.07%, 0.05%, 0.05%, 0.17% and 0.10% observed below 700°C just for the Himalayan salt sample (see figure 5b). Below about 400°C, the DSC signal showed endothermic effects which correlate – and which are due to the mass-loss steps; details like peak temperatures and enthalpies can be seen in figure 5b. The mass loss below about 200°C is most probably due to the release of moisture and the dehydration of gypsum (mixture of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) with an estimated concentration in the sub percent range. Between about 200°C and 400°C, the mass-loss steps could be due to the decomposition of various carbonates while the mass-loss step in the range of 450°C could be due to the dehydration of $\text{Ca}(\text{OH})_2$. For further interpretations of the mass-loss steps, evolved gas analysis would clearly be helpful [8]. The DSC result at

above about 580°C is also very complex (see figure 5b): At least seven endothermic DSC effects were detected. The main peak at 799°C is again most probably due to a binary, NaCl-rich mixture such as NaI-NaCl, KCl-NaCl [7] or Na_2CO_3 -NaCl [7, 9], from where the DSC peak at 712°C may also originate. The remaining DSC effects between 580°C and 720°C are presumably due to the melting processes of several iodides, fluorides, chlorides, carbonates or sulfates and mixtures of them with NaCl or KCl [7, 10]. For example, the DSC peak at 587°C could be due to CaI_2 or K_2SO_4 , the sharp peak at 690°C might be due to KI and the peak at 679°C could be due to a structural transformation of Fe_2O_3 [10]. Further details like peak temperatures and enthalpies can again be seen in figure 5b. The mass loss of the Himalayan salt of 2.74% above 700°C (see figure 5a), which is again due to partial evaporation, is significantly higher than that of the other samples investigated.



5b Temperature-dependent mass change (TGA) and heat flow rate (DSC) of the Himalayan salt sample (partial view in enlarged scaling)

Conclusion

Investigations of NaCl, KCl, table salt and Himalayan salt by means of the STA 449 *F5 Jupiter*[®] demonstrated that this instrument is well suited for studying substances such as alkali salts and mixtures of them. Particularly the DSC signal, which very clearly reflects melting processes and other phase transformations, allows for an investigation of phase diagrams via melting temperatures and even enthalpies. The TGA signal indicates not only evaporation of the sample but also mass-loss steps due to the decomposition of, for example, impurity substances which can be identified and quantified in several cases.

Literature

[1] S. Yalcin and I.H. Mutlu, Structural Characterization of Some Table Salt Samples by XRD, ICP, FTIR and XRF techniques, *Acta Physica Polonica A*, Vol. 121, 2012, p.50-52
 [2] V. K. Klassen and E. P. Ermolenko, Problem of Impurity of Salts of Alkali Metals in Cement Raw Materials, *Middle-East Journal of Scientific Research* 17 (8), 2013, p. 1130-1137
 [3] T. Bauer, D. Laing and R. Tamme, Characterization of Sodium Nitrate as Phase Change Material, *International Journal of Thermophysics* 33, 2012, p.91-104

[4] Caesar & Loretz GmbH, Herderstr. 31, D-40721, Germany
 [5] Euro OTC Pharma GmbH, Edisonstr. 6, D-59199 Bönen
 [6] O. Knacke, O. Kubaschewski, K. Hesselmann, *Thermochemical properties of inorganic substances*, Springer-Verlag, Berlin, 1991.
 [7] FTSalt – FACT Salt Phase Diagrams, Ecole Polytechnique de Montreal, available at http://www.crct.polymtl.ca/fact/documentation/FTsalt/FTsalt_Figs.htm
 [8] A. Schindler, G. Neumann, A. Rager, E. Füglein, J. Blumm and T. Denner, A novel direct coupling of simultaneous thermal analysis (STA) and Fourier transform-infrared (FT-IR) spectroscopy, *Journal of Thermal Analysis and Calorimetry* 113, 2013, p.1091-1102, freely available at <http://link.springer.com/article/10.1007%2Fs10973-013-3072-9>
 [9] K. Iwasawa, S. Yamaguchi and M. Maeda, Phase Relation and Thermodynamic Properties of NaCl-Na₂CO₃ System as a Basic System for Secondary Fly Ash in Incineration Processes of Municipal Wastes, *Materials Transactions* 42, 2001, p. 2480-2486
 [10] D'Ans Lax, *Taschenbuch für Chemiker und Physiker*, Springer Verlag, Berlin, 1967